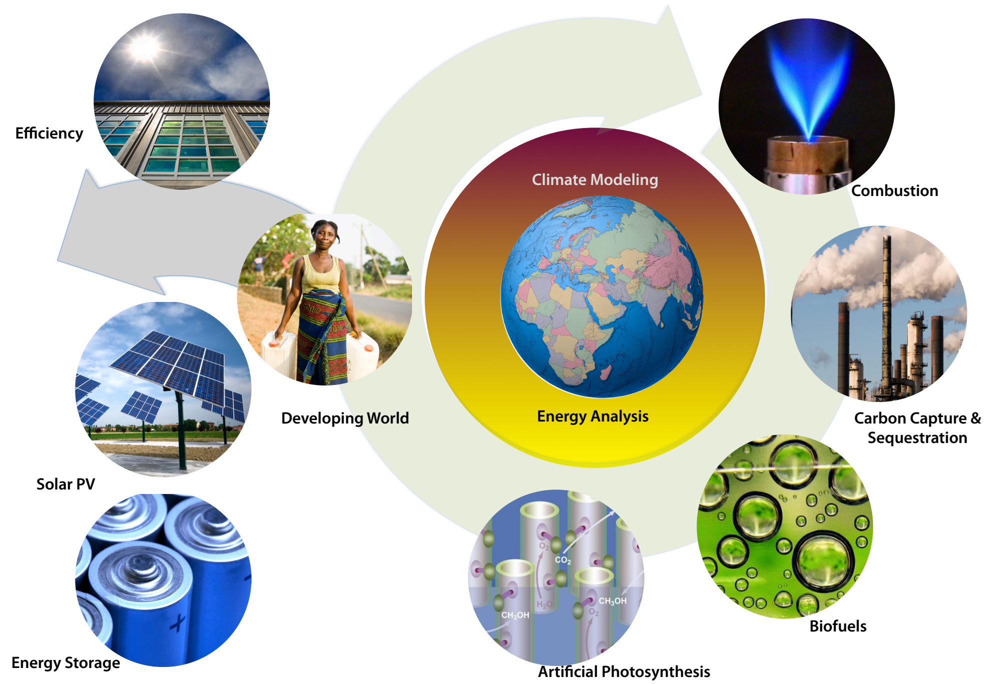
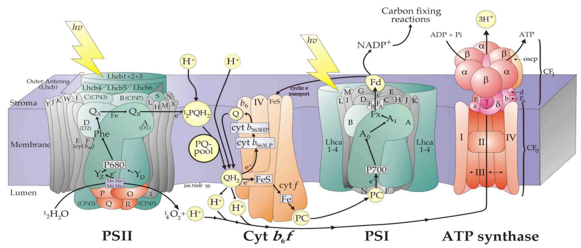
Carbon Cycle 2.0 Initiative

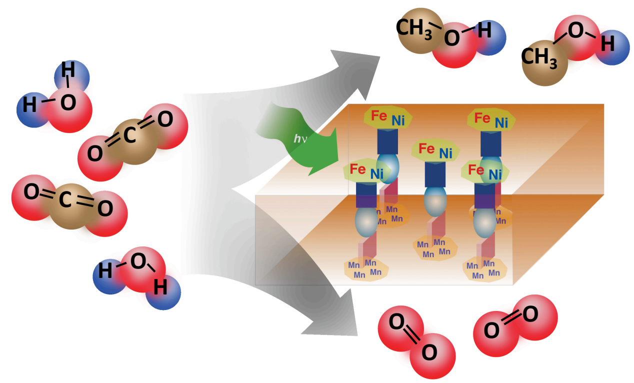


Solar Energy Research Center
Artificial photosynthesis



Actual photosynthetic apparatus

Artificial Photosynthesis



Solar Technology Evolution

Solar Thermal:

Harness heat

Steam engine

~25 meV

Single Gap Photovoltaic:

Silicon and Thin Film

~1eV

Photoelectric effect

Up to 24% efficiency

$4-5/W

Multigap cells:

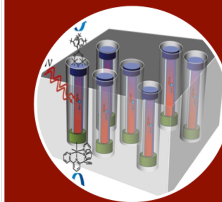
Semiconductor processing

Artificial materials

~Up to 40% efficiency

$350-1000s$/W

Concentration?



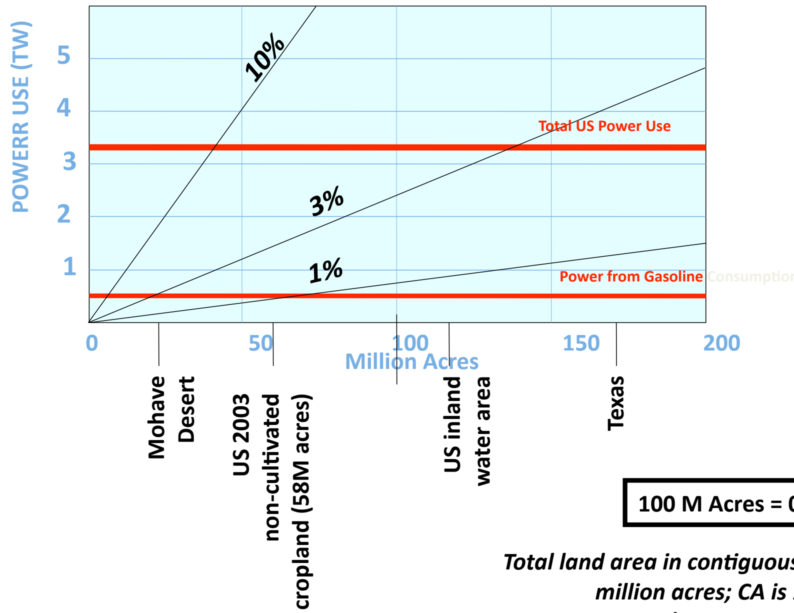
Solar Fuel:

Control of Entropy

Energy Storage

climbing the thermodynamic ladder

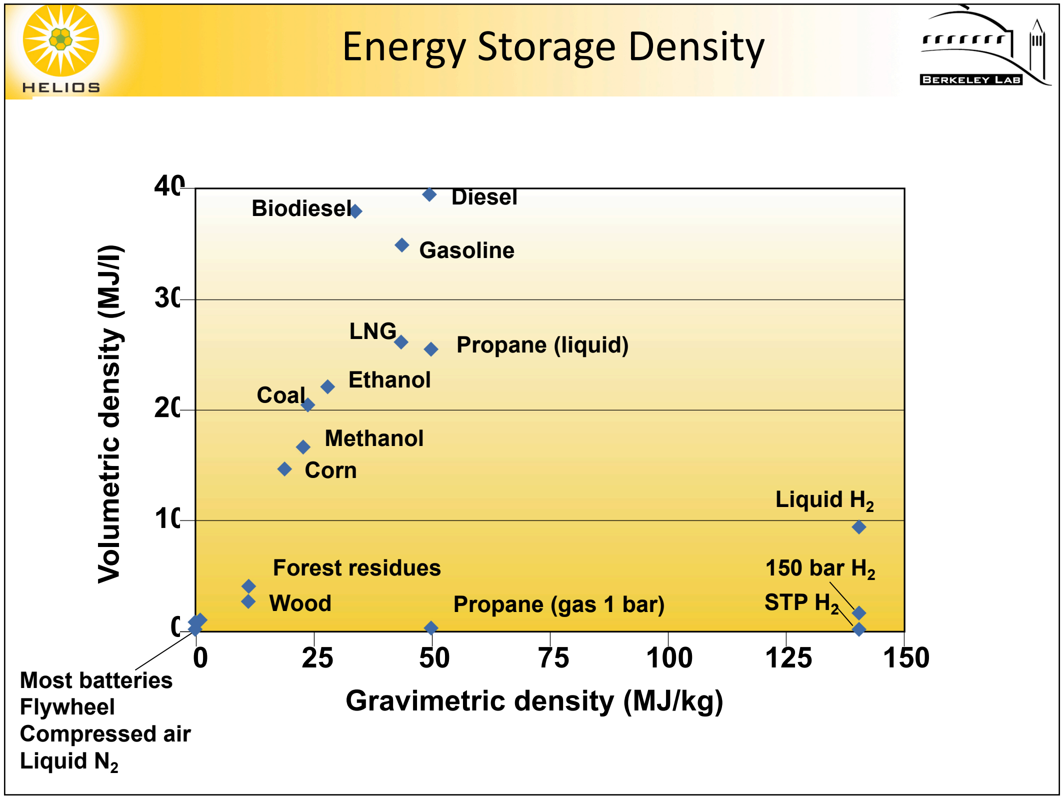
Solar Efficiency and Land Usage, USA



100 M Acres = 0.4 M Sq Km

Total land area in contiguous US is 2,248 million acres; CA is 105 M acres (~99.8 M acres dry land)

Energy Storage Density



Photochemical water splitting

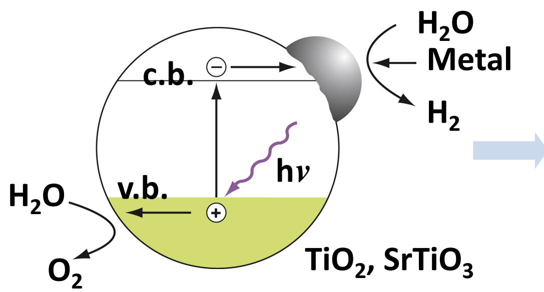
Photochemical water splitting to H_2 and O_2 at semiconductor materials

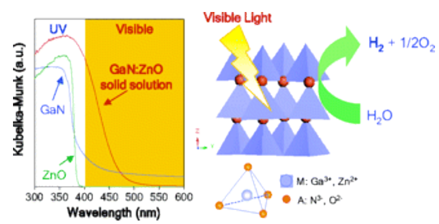
First complete water photoelectrolysis system at n-TiO_2 ($SrTiO_3$) with UV light:

A. Fujishima, K. Honda, *Nature* **238**, 37 (1972)
M.S. Wrighton, *J. Am. Chem. Soc.* **98**, 2774 (1976)

State of the art single bandgap material for overall water splitting with visible light:
Q.E. = 2.5% at 430 nm

K. Domen, Nature 440, 295 (2006)





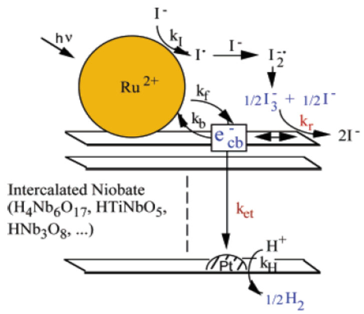
Challenges not yet met: Efficiency under visible light is very low
No separation of hydrogen from oxygen
Co-catalysts made of noble metals

Integrated photo-conversion systems

Visible light to chemical energy conversion in hierarchical membrane or scaffold with separation of products in compartmentalized spaces

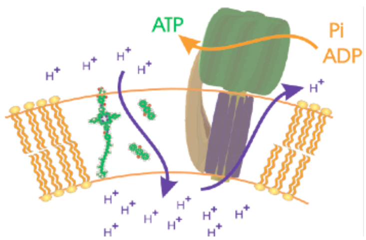
Splitting of HI to H_2 and I_2 in hard matter scaffold (layered Ti niobate)

T.E. Mallouk et al., *J. Phys. Chem. B* **101**, 2508 (1997)



Efficient conversion of sunlight to chemical energy in soft matter membrane (lipid bilayer)

A.L. Moore, D. Gust, T.A. Moore, *Nature* **392**, 479 (1998)

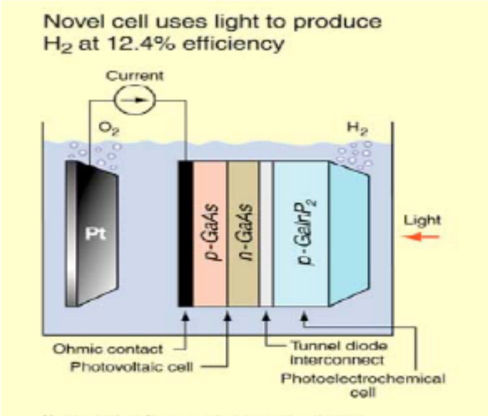


Challenges not yet met:

- **Efficiency under visible light is very low**
- **No water splitting**
- **Co-catalyst and sensitizer made of noble metals**

Efficient solar water splitting to H_2 and O_2 in photoelectrochemical cell

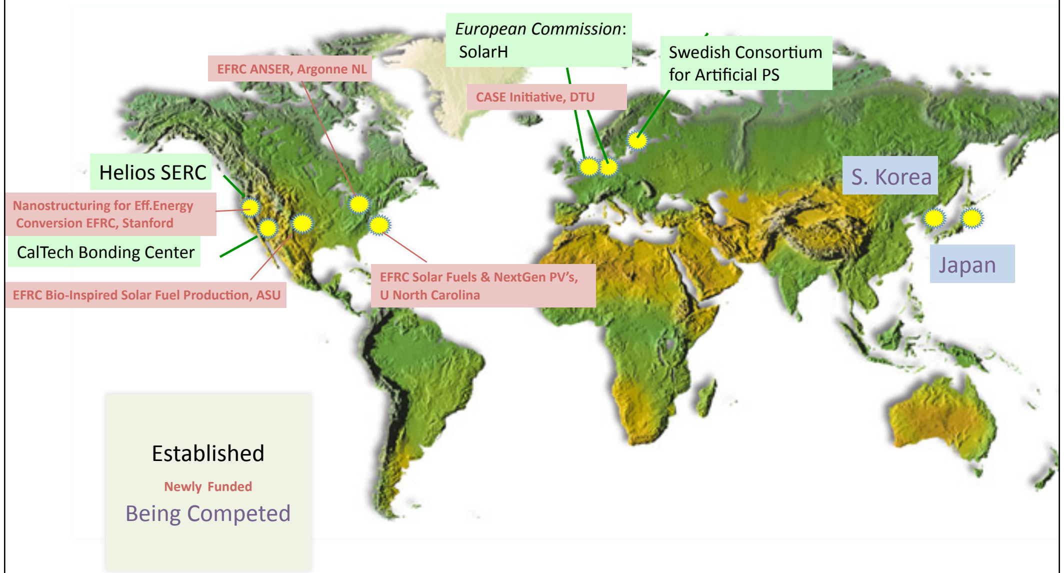
Efficient solar water splitting (12% overall efficiency)



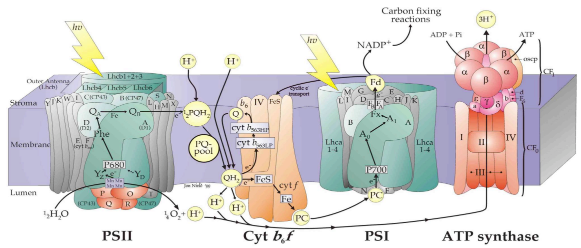
O. Khaselev, J. Turner, *Science* **280**, 425 (1998)

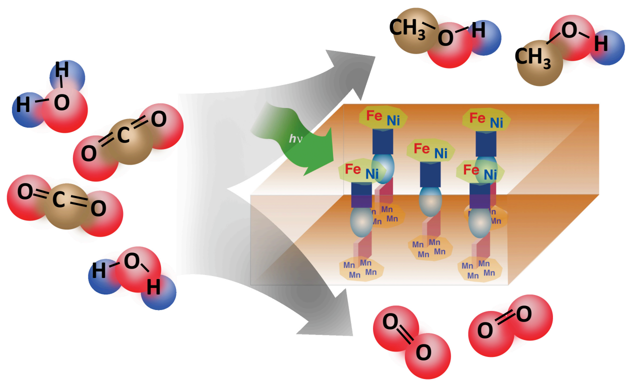
Challenges not yet met: Materials and synthetic process not scalable
Materials not durable

Solar Fuels Centers Around The World



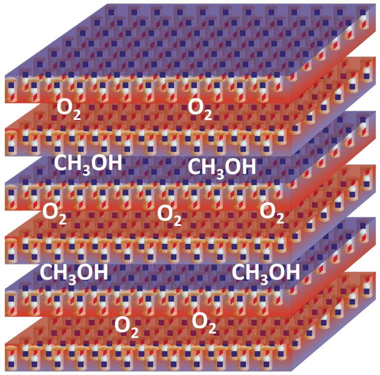
Why Nano?





- **High density of reactants (photo-generated charges) leads to more products**
- **10 k_BT dissipation required to ensure directionality of energy flow**
- **Match solar flux**

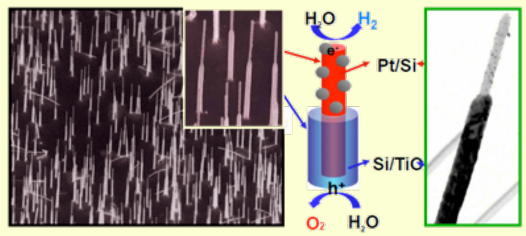
Match catalytic activity with solar flux



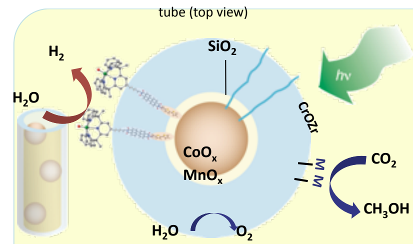
Planes of membranes holding vertically aligned PV elements with catalysts attached top and bottom

- The solar flux is 2 to 5 kwH/m^2/day
- This corresponds to ~1500 solar photons/ nm^2/sec at peak
- To match this flux, we need to arrange catalysts with an areal density and turnover rate of 100-200/nm^2/sec

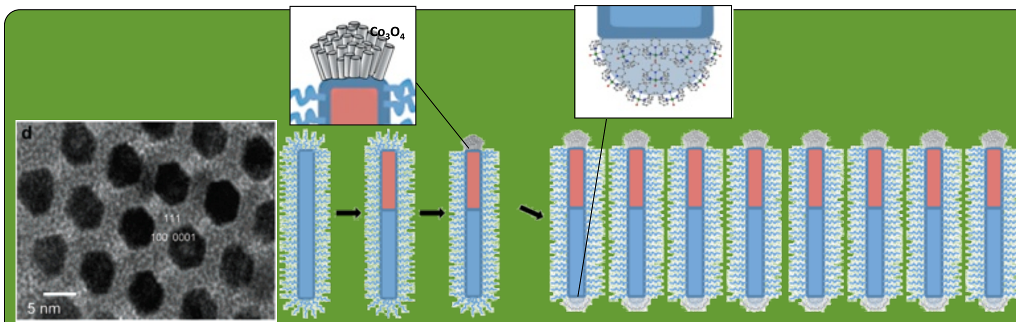
Helios SERC : 3 prototype artificial photosynthetic units



Forest of concentric cylindrical nanotubes

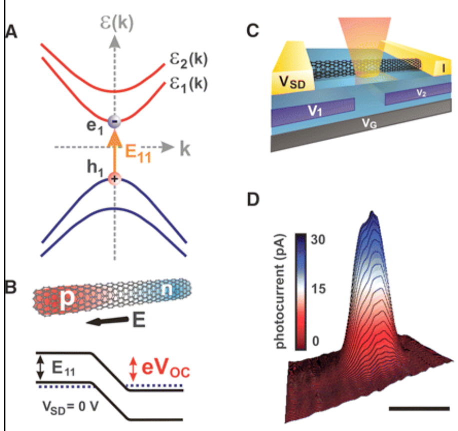


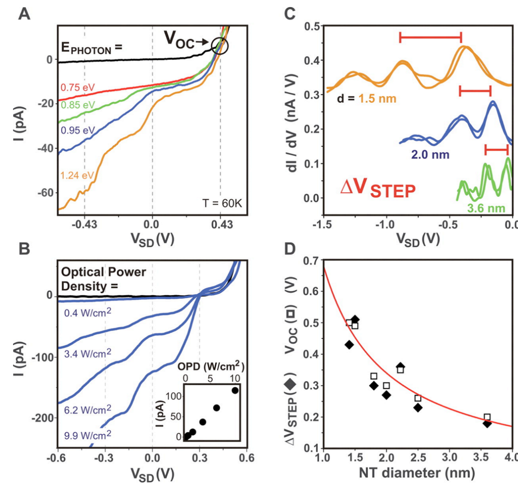
Catalyst-in-tube design with nanocrystal catalyst



Segmented colloidal nanorod membrane with catalysts attached

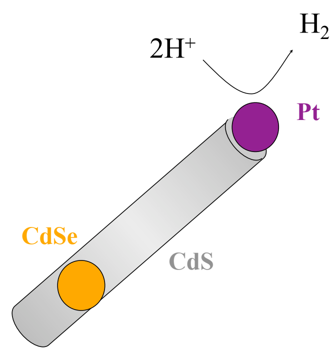
renewed interest in multi-exciton generation

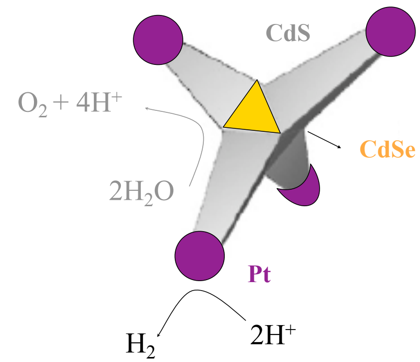




Author(s): Gabor, NM (Gabor, Nathaniel M.); Zhong, ZH (Zhong, Zhaohui); Bosnick, K (Bosnick, Ken); Park, J (Park, Jiwoong); McEuen, PL (McEuen, Paul L.)
Title: Extremely Efficient Multiple Electron-Hole Pair Generation in Carbon Nanotube Photodiodes
Source: SCIENCE, 325 (5946): 1367-1371 SEP 11 2009

Hydrogen production from seeded rods w/ Pt

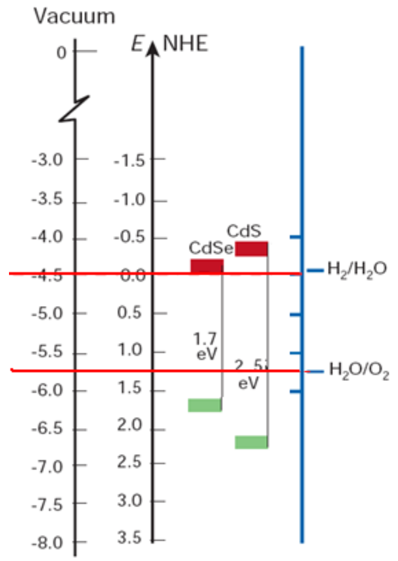




CdS/Pt systems:
Ningzhong Bao, Liming Shen, Tsuyoshi Takata, and Kazunari Domen *Chem. Mater.*, **2008**, 20 (1), 110-117
Jean Francois Reber, and Milos Rusek *J. Phys. Chem.*, **1986**, 90 (5), 824-834

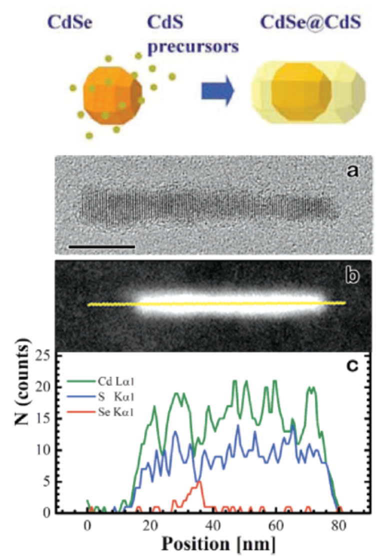
Lilac Amirav

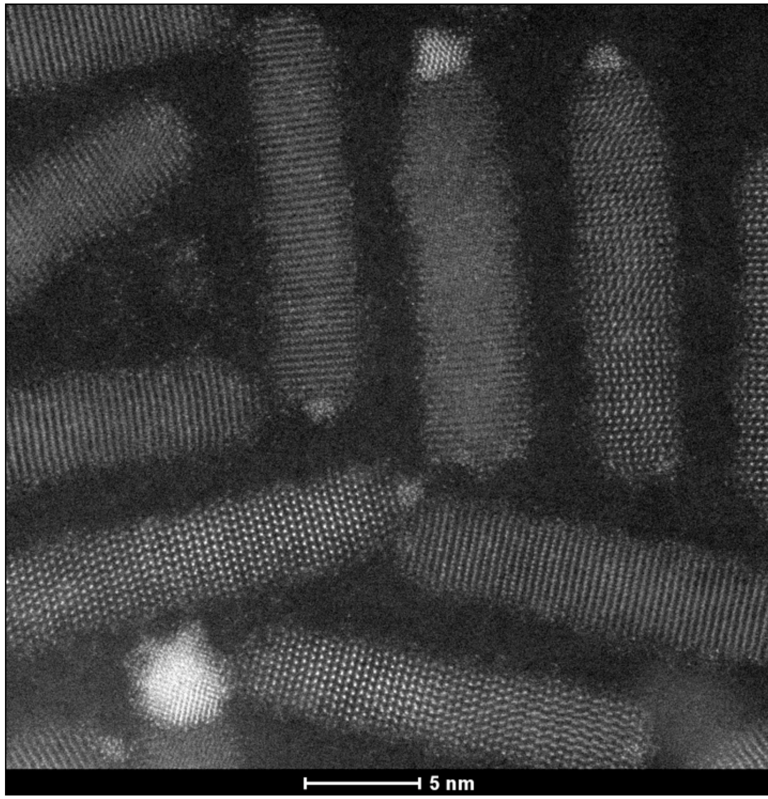
CdSe/CdS Nanoheterostructures



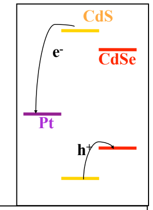
Talapin [2003+2007], Carbone [2007]

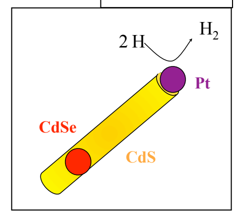
Weller Manna Banin Feldman



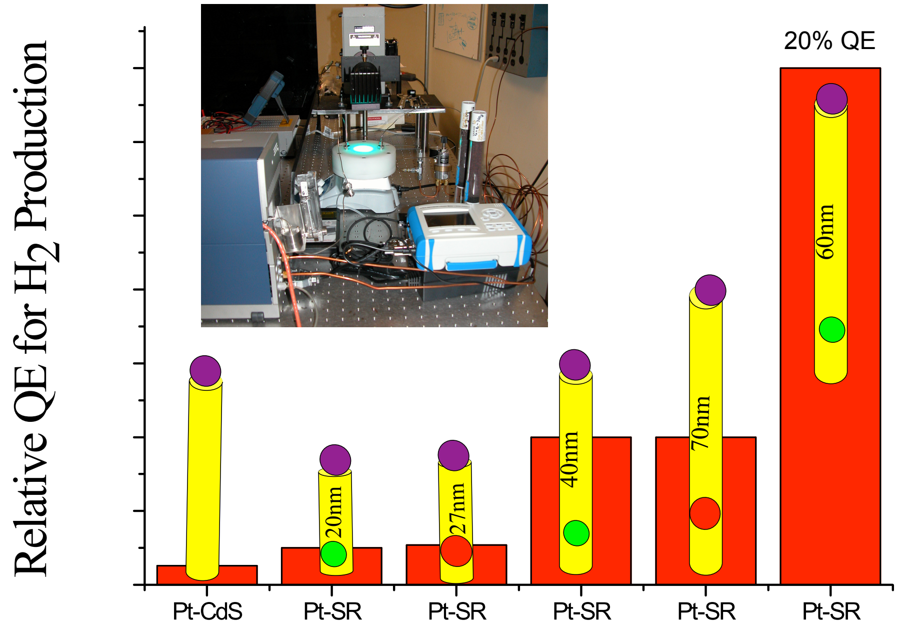


Pt growth
on the tips
of the
seeded
nanorods

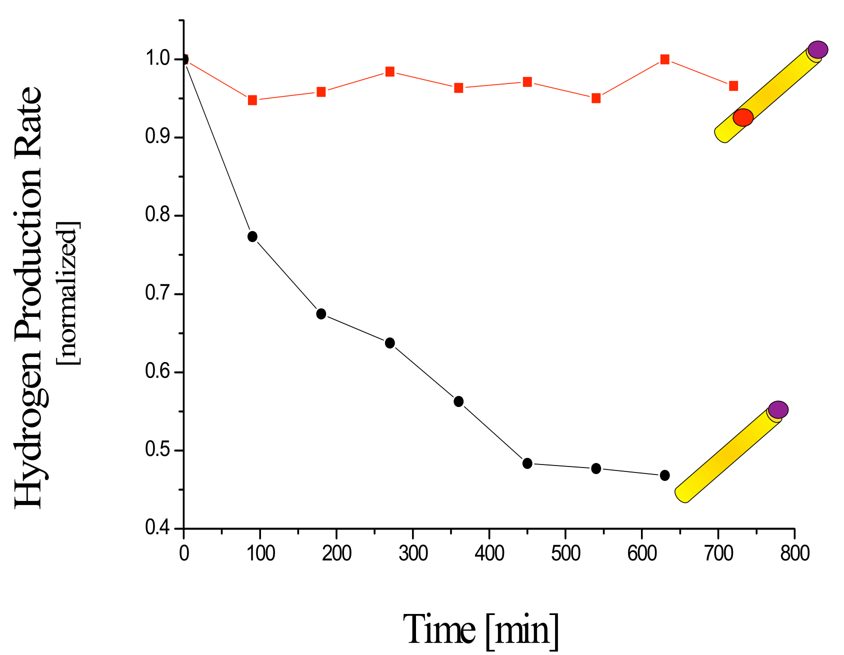




Improved Photocatalytic Efficiency With Longer Rods and Smaller Seeds

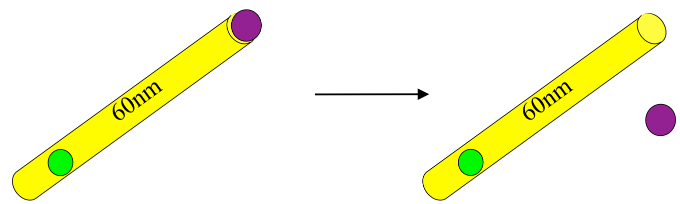


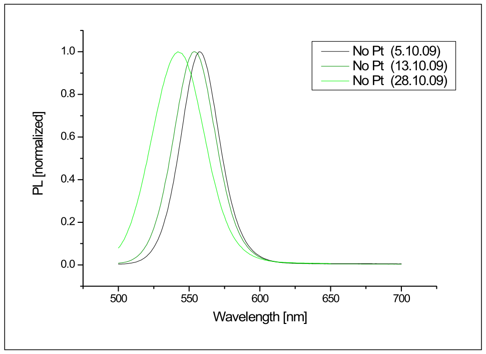
Seeded CdSe@CdS w/Pt is significantly more stable than CdS w/Pt

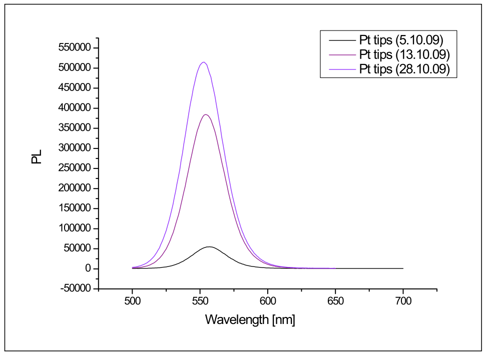


Stability

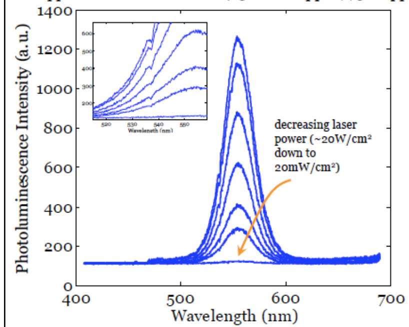
The interface between the semiconductor and the metal is the first to degrade





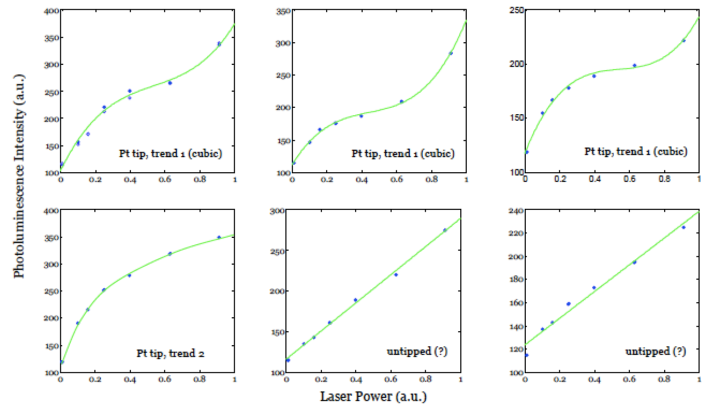


Pt-tipped seeded rod solution (25% non-tipped, 75% tipped)



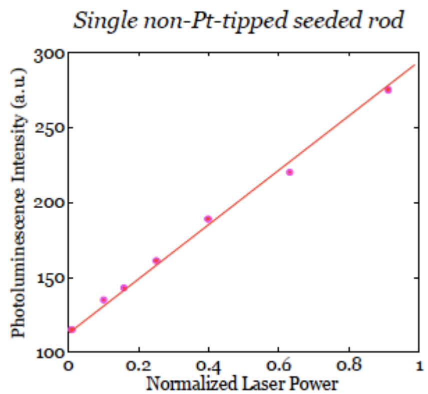
Power Dependence of PL from seeded rods with Pt tips

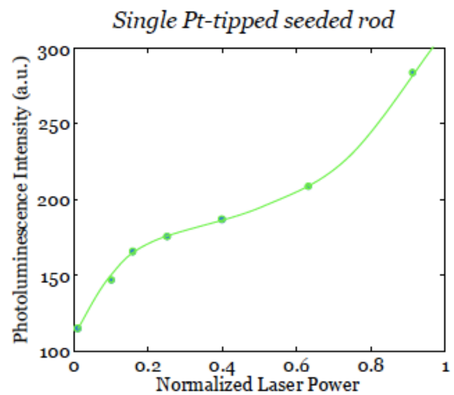
Collected from single rods from Pt-tipped solution (25% not tipped)

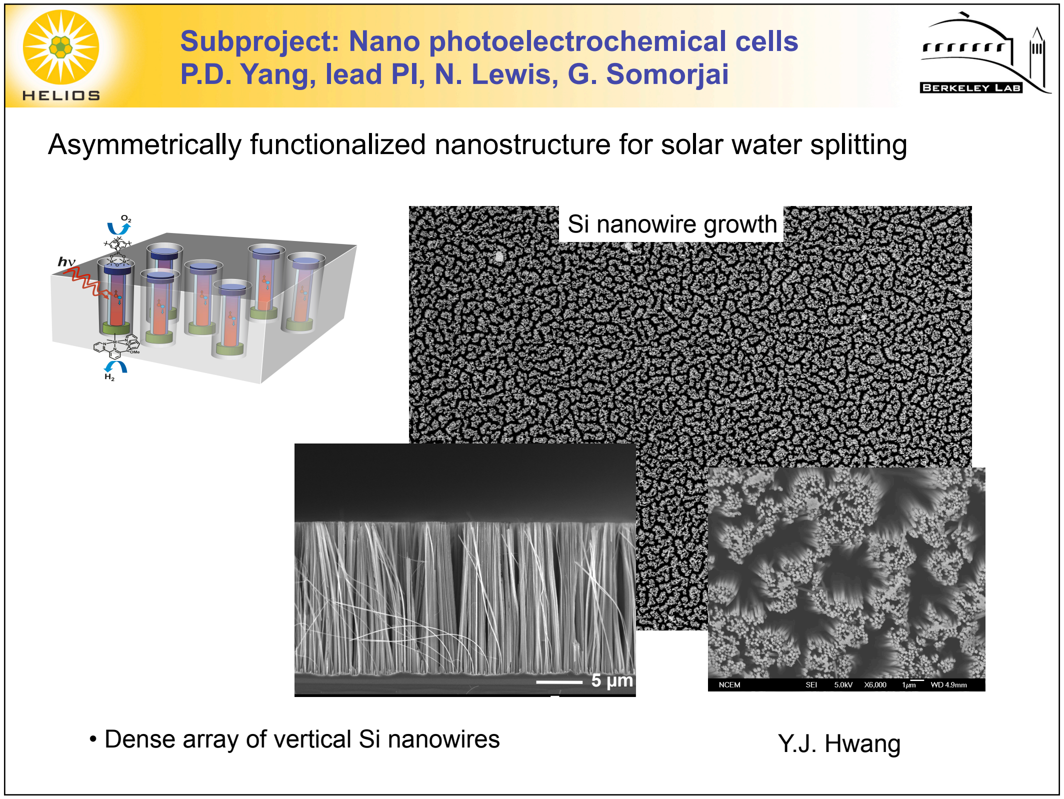


Jennifer Dionne
and Lilac Amirav

Single particle data (λ_{exc}=457 nm)







Peidong Yang and co-workers: Heterojunction nano photovoltaic assembly asymmetrically functionalized with water splitting catalysts

The goal of this work is to make nanoscale photoelectrochemical cells made of a semiconductor heterojunction and to then functionalize the anode and cathode selectively with water oxidation or proton reduction catalysts. The heterojunction design has several important features: Enables use of two solar photons, which results in better use of energy from the solar spectrum compared to a single bandgap absorber and affords the required band energies for water oxidation and proton reduction. Also, the design lends itself to asymmetric functionalization of the nano PV elements by oxidation and reduction catalysts. The nano PEC cells will ultimately be arranged with defined orientation in a membrane to achieve separation of the hydrogen from the evolving oxygen.

Explanation of the slide: A highly oriented nanowire array of Si/TiO_2 core/shell nanorods was prepared using an aqueous electroless etching method followed by synthesis of the TiO_2 shell by atomic layer deposition. By selectively protecting one half of the array with an organic polymer, TiO_2 was chemically edged away from the unprotected section. This resulted in an array of Si/TiO_2 nanorods in which one half of each rod had the Si exposed (cartoon in center of slide, SEM in green box). The image on the left shows a section of the array. The exposed Si section was subsequently functionalized with Pt dots by reducing Pt ions from solution (acidic solution of H_2PtCl_6) electrochemically at the Si cathode.

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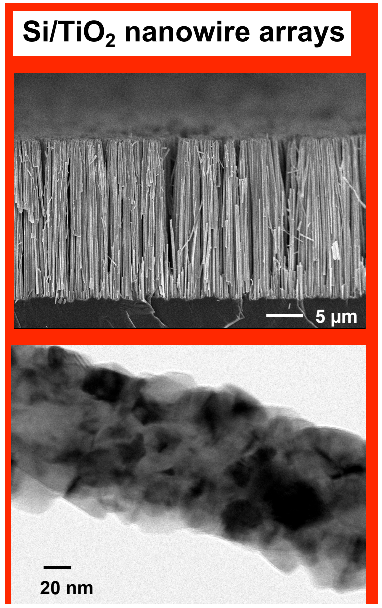
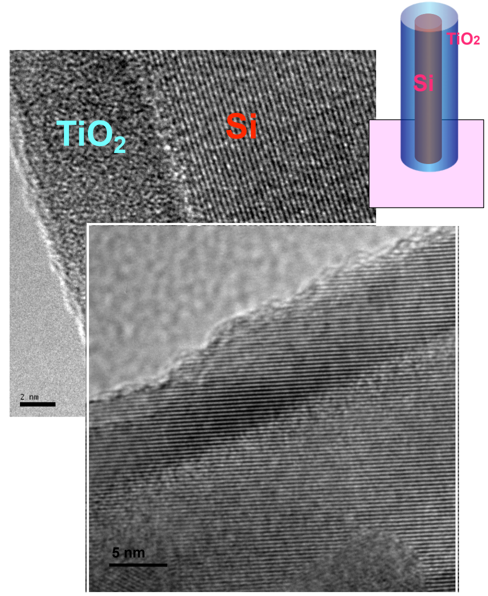
Si/TiO_2 core/shell nanowires

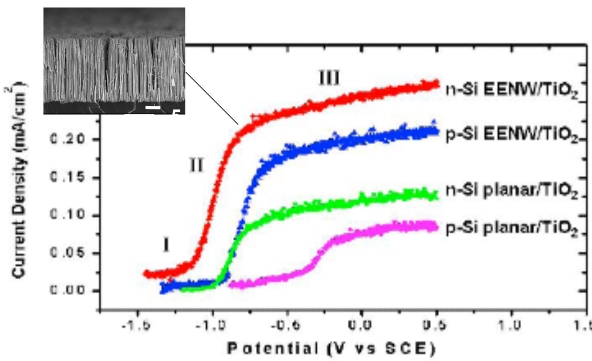


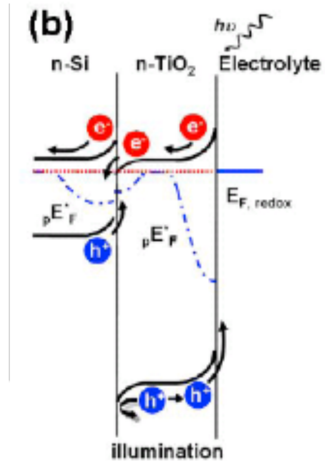


- Polycrystalline TiO_2 (anatase) shell by ALD

n-Si/n-TiO_2 core-shell nanowires

Enhanced Photoactivity



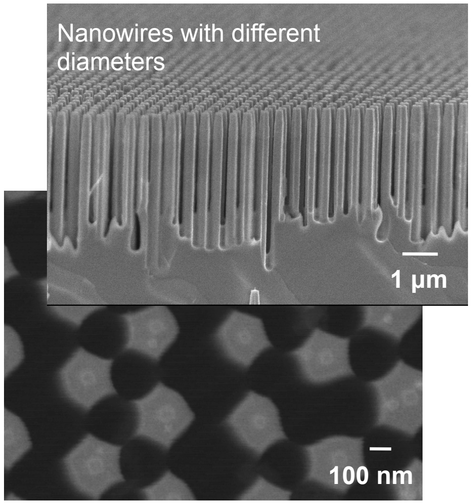


- Si/TiO_2 core/shell nanowire array shows enhanced photoactivity compared to TiO_2 thin film on planar Si substrate

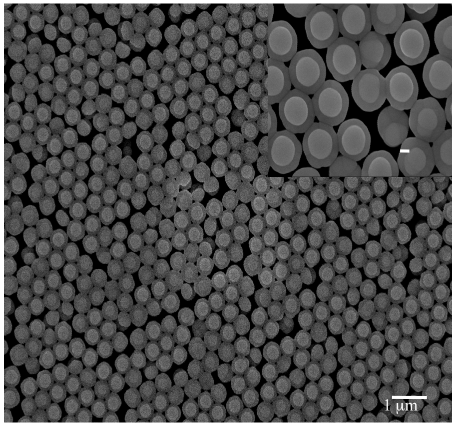
Y.J. Hwang, A. Boukai, P.D. Yang, *Nano Lett.* **9**, 410 (2009)

Future work: Photoactivity of Si/TiO_2 core-sheath nanostructure

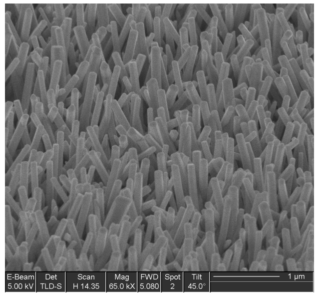
- Dependence on dopant level and nanowire diameter
- Embedding Si pn junctions or even tandem pn junctions, for direct solar H_2O splitting



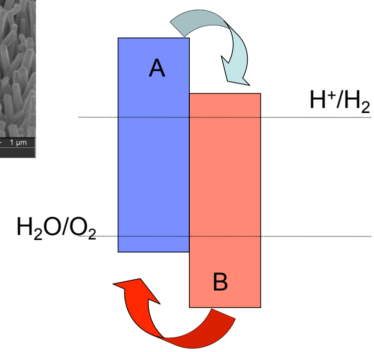
Si core-shell solar cell, 3.9%

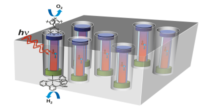


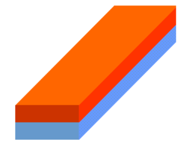
Future work: Improved version of semiconductor heterostructure design



- Type II A/B semiconductor
- Both E_g about 1.5-2 eV
- Nanotape or core-shell geometry



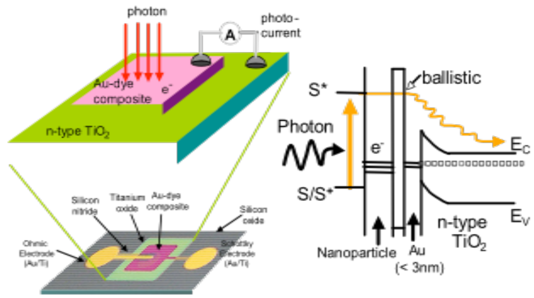


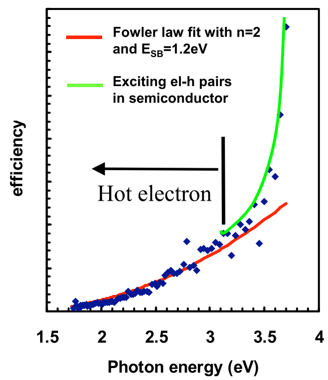


Possible candidates: InGaN nanowires with 30-50% In side-coated with doped Fe_2O_3

P. Yang et al., *Nano Lett.* **2**, 1109 (2002); *Nature Mater.* **6**, 951 (2007)
M. Graetzel et al., *J. Am. Chem. Soc.* **128**, 4582 (2006)

Future work: Hot electron injection for improved photon to fuel conversion efficiency

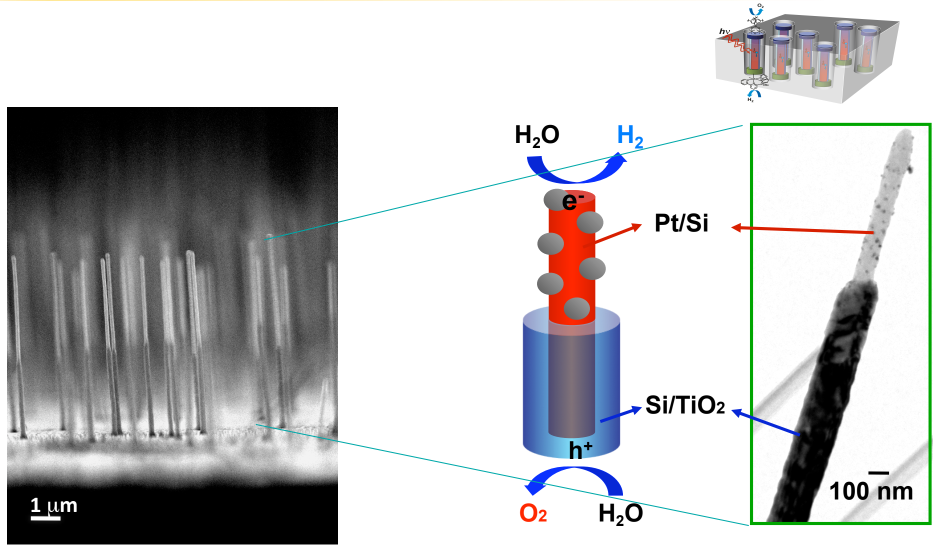




J. Park, G. Somorjai, *Chem. Phys. Chem.* **7**, 1409 (2006)

- Expansion of the range of photons for charge carrier generation to longer visible wavelengths using organic dyes on ultra thin metal layers
- Exploration of Schottky diodes with low barriers, e.g. Ag/GaN, $AgTiO_2$, Pt/Si

Future Work: Asymmetrical nanostructure



Y.J. Hwang, A. Boukai, P.D. Yang, *Nano Lett.* **9**, 410 (2009)

- Pt decorated Si/TiO_2 asymmetric nanowire array which can separate reduction and oxidation reactions

Peidong Yang and co-workers: Heterojunction nano photovoltaic assembly asymmetrically functionalized with water splitting catalysts

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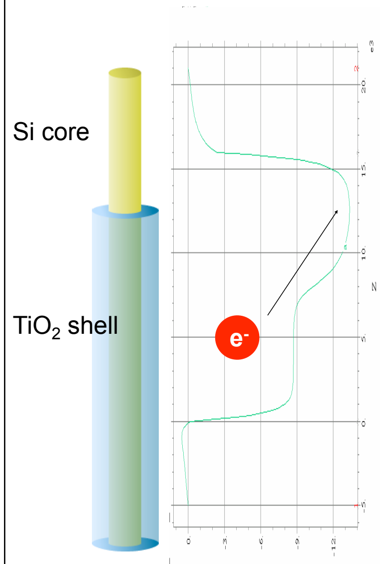
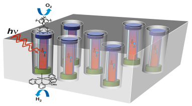
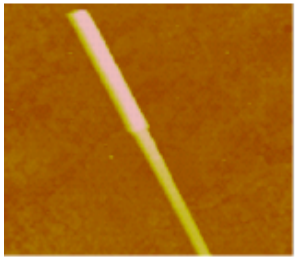
Future work: Scanning Kelvin probe microscopy characterization of Si/TiO_2 asymmetric nanostructure



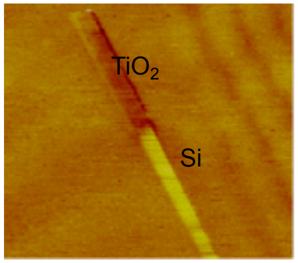
L. W. Wang
Simulation



- Examine longitudinal potential difference
- Charge separation across interface/junction



Topographic image

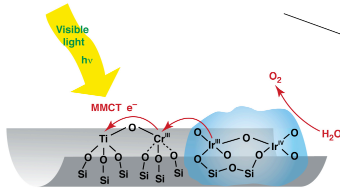


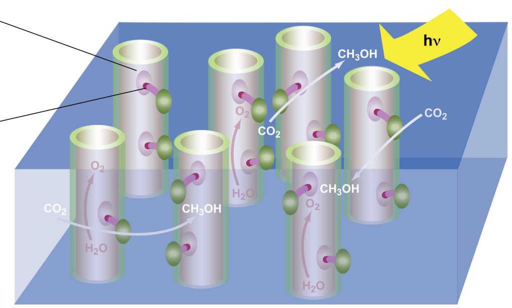
Potential image

Subproject: Polynuclear photocatalytic units coupled in nanoporous silica scaffolds

H. Frei, lead PI, V. Yachandra, D. Tilley, L-W. Wang

unsymmetrical silica nanotube array



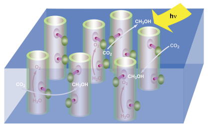


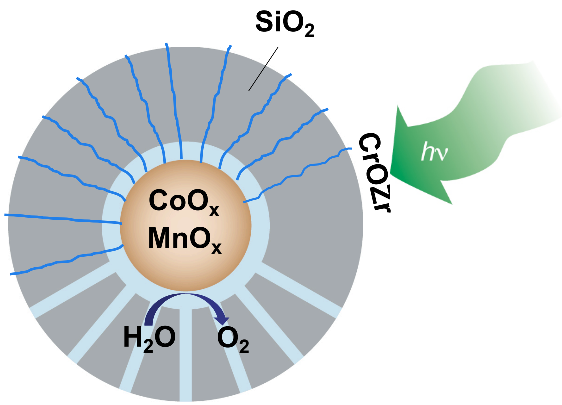
Photocatalytic unit for visible light H_2O oxidation
Quantum yield $\geq$ 14%

Han, Frei, *J. Phys. Chem. C* **112**, 16156 (2008)
Nakamura, Frei, *J. Am. Chem. Soc.* **128**, 10668 (2006)
Lin, Frei, *J. Am. Chem. Soc.* **127**, 1610 (2005)

- Robust all-inorganic photocatalytic units for two half reactions coupled across silica wall

First goal: Proof of concept using catalyst core/ silica shell construct





Tasks:

- Demonstrate core/ shell assembly for driving catalysis by a sensitizer positioned on the outside
- Develop hole (or electron) conducting nanowires embedded in silica

HELIOS

Ir is least abundant metal on earth, need catalysts made of 1st row transition metals

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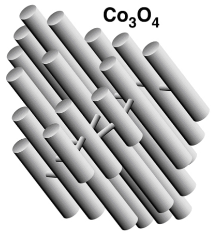
Turnover frequencies (TOF) for oxygen evolution at Co and Mn oxide materials reported in the literature

Oxide	TOF (sec^{-1})	Overvoltage, η (mV)	pH	T (°C)	Quantum yield	Reference
Co_3O_4 [1]	0.035	325	5	RT	58%	Harriman (1988)
Co_3O_4	≥ 0.0025	350	14	30	--	Tamura (1981) [2]
Co_3O_4	≥ 0.020	295	14	120	--	Wendt (1994) [3]
Co_3O_4	≥ 0.0008	414	14.7	25	--	Tseung (1983) [4]
Co_3O_4	≥ 0.006	235	14	25	--	Singh (2007) [5]
Co,P film	≥ 0.0007	410	7	25	--	Nocera (2008) [6]
MnO_2	≥ 0.013	440	7	30	--	Tamura (1977) [7]
Mn_2O_3	0.055	325	5	RT	35%	Harriman (1988) [1]

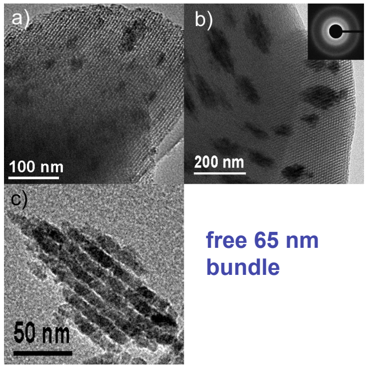
[1] Harriman, A.; Pickering, I.J.; Thomas, J.M.; Christensen, P.A. *J. Chem. Soc., Farad. Trans. 1* **1988**, *84*, 2795-2806.
[2] Iwakura, C.; Honji, A.; Tamura, H. *Electrochim. Acta* **1981**, *26*, 1319-1326.
[3] Schmidt, T.; Wendt, H. *Electrochim. Acta* **1994**, *39*, 1763-1767.
[4] Rasiyah, P.; Tseung, A.C.C. *J. Electrochem. Soc.* **1983**, *130*, 365-368.
[5] Singh, R.N.; Mishra, D.; Anindita; Sinha, A.S.K.; Singh, A. *Electrochem. Commun.* **2007**, *9*, 1369-1373.
[6] Kanan, M.W.; Nocera, D.G. *Science* **2008**, *321*, 1072-1075.
[7] Morita, M.; Iwakura, C.; Tamura, H. *Electrochim. Acta* **1977**, *22*, 325-328.

Nanostructured Co oxide cluster in mesoporous silica scaffold

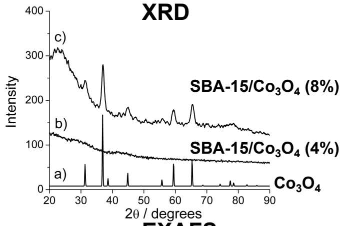
Synthesis of Co oxide clusters in SBA-15 using wet impregnation method

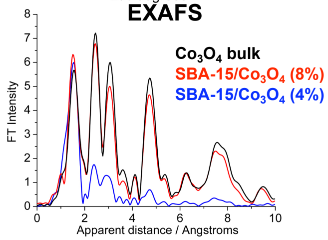


35 nm bundles (4 % loading) **65 nm bundles (8 % loading)**



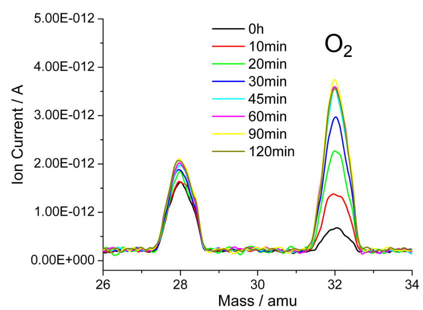
free 65 nm bundle

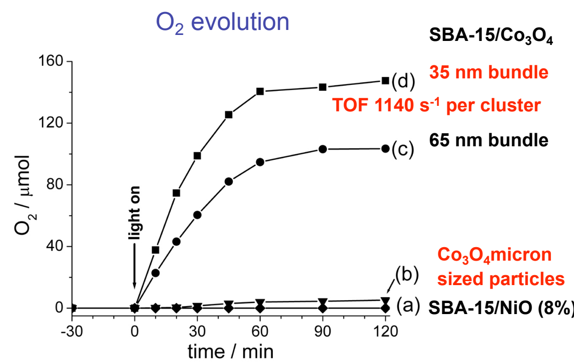




- Co oxide clusters are 35 nm bundles of parallel nanorods (8 nm diameter) interconnected by short bridges
- XRD and EXAFS reveal spinel structure

Efficient oxygen evolution at Co_3O_4 nanoclusters in SBA-15 in aqueous suspension



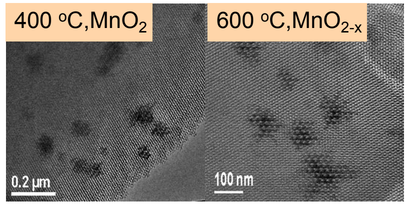


F. Jiao, H. Frei, *Angew. Chem. Int. Ed.* **49**, 1841 (2009)

- Visible light water oxidation in aqueous SBA-15/Co_3O_4 suspension using $Ru^{2+}(bpy)_3$ + $S_2O_8^{2-}$ method. Mild conditions: 22°C, pH 5.8, overvoltage 350 mV
- High catalytic turnover frequency: 1140 O_2 molecules per second per cluster, suitable for integrated system matching solar flux
- O_2 yield is 1600 times larger for 35 nm bundle catalyst compared to µ-sized Co_3O_4; Surface area of nanorod bundle cluster = factor of 100, catalytic efficiency of surface Co centers = factor of 16

Nanostructured Mn oxide clusters supported on mesoporous silica KIT-6

TEM images for KIT-6 supported Mn oxide nanoclusters

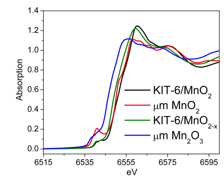


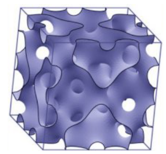
Cluster size obtained from TEM data:

KIT-6/MnO_2 ~75nm

KIT-6/MnO_{2-x} ~95nm

XAFS

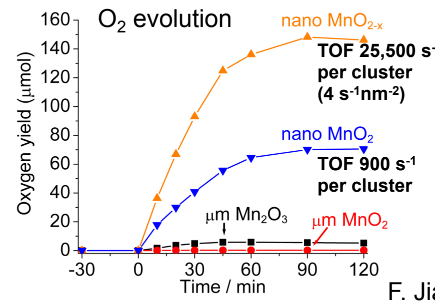




KIT-6 (3D channels)

MnO_2:
Crystalline β-MnO_2 (rutile) (EXAFS)

MnO_{2-x}:
Mixed Mn oxide (EXAFS, XANES)

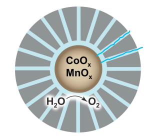


F. Jiao

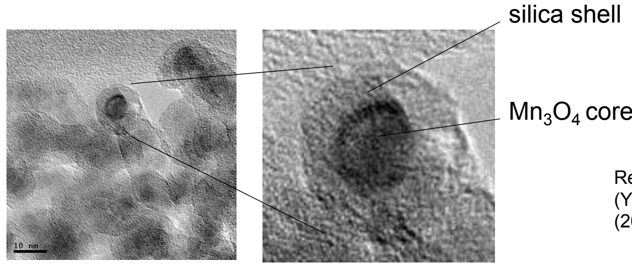
- Spherical Mn oxide cluster (MnO_{2-x}) with turnover frequency of 25,500 s^{-1}(4 $s^{-1}nm^{-2}$)
- Suitable for integrated system achieving TOF of 100 $s^{-1}nm^{-2}$

Future work: Proof of concept for driving water oxidation catalyst with chromophore separated by silica wall

Co or Mn oxide/ silica core shell constructs with nanowires penetrating the SiO_2 shell



Mn oxide core/ silica shell construct



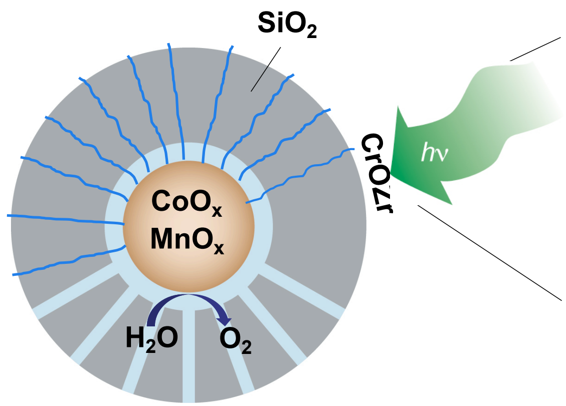
Reverse microemulsion method (Ying, J.Y., *Langmuir* **24**, 5842 (2008))

F. Jiao

Main tasks:

- Replace capping agents with hole-conducting organic tails, e.g. oligo (p-phenylene vinylene)
- Verify charge transport contact through organic wire across silica shell by transient optical spectroscopy using a visible light sensitizer for hole injection
- Demonstrate water oxidation activity

Future work: Asymmetric assembly of binuclear charge transfer chromophore, coupling to water oxidation catalyst



Covalent linkage of wire with Cr donor center through 1,3 dipolar addition ('click') of termi on wire and a ligand of Cr(NCCH$_3$)$_n$

termi:
-N$_3$ + acetylene, or
-CNO + acetylene

Main tasks:

- Couple binuclear charge transfer chromophore on the outside silica wall to the nanowire by click chemistry
- Evaluate photocatalytic assembly by water oxidation catalysis and transient optical spectroscopy

Future work: Closing the photocatalytic cycle by coupling charge-transfer chromophore to a CO_2 reducing photocatalyst

HELIOS

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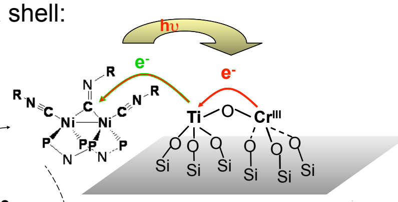
Coupling charge-transfer chromophore to Ni dimer catalyst for CO_2 reduction

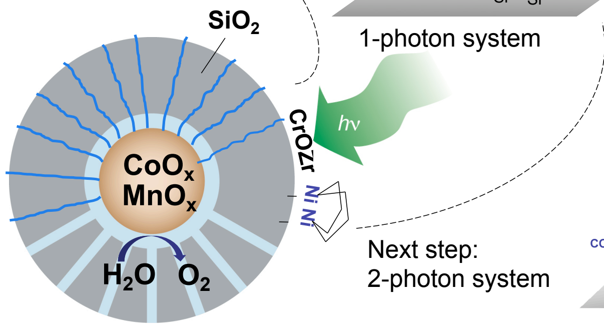
Outside surface of silica shell:

C. Kubiak's CO_2 reduction catalyst (TOF = 1 s^{-1})

$CO_2 \rightarrow CO$

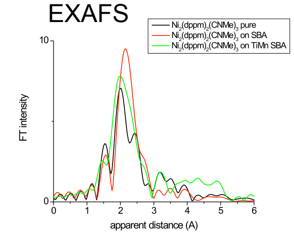


1-photon system

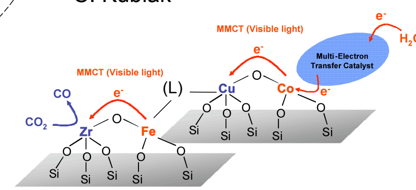


Next step:
2-photon system

EXAFS



W. Weare, J. Yano, V. Yachandra, C. Kubiak

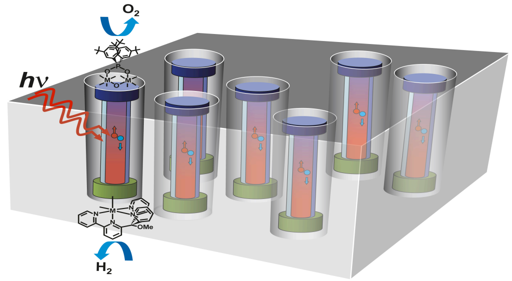


W. Weare, Y. Pushkar, V. Yachandra, H. Frei
J. Am. Chem. Soc. **130**, 11355 (2008)

- Coupling of molecular or cluster CO_2 reduction catalyst to binuclear chromophore
- Assembly of 2-photon system on the outer surface of silica shell

Subproject: Polyelectrolyte and block-copolymer membrane systems

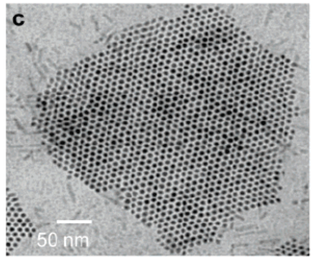
R.A. Segalman, lead PI

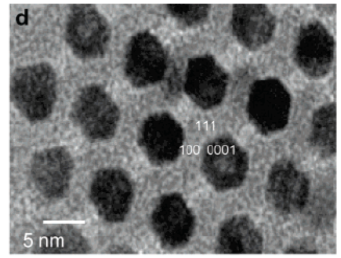


Integrated membrane requirements:

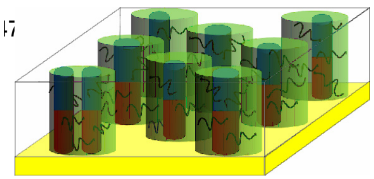
- Integration of components with defined orientation
- Facile proton transport
- Minimizing gas back diffusion
- Techniques must be flexible for components currently in development

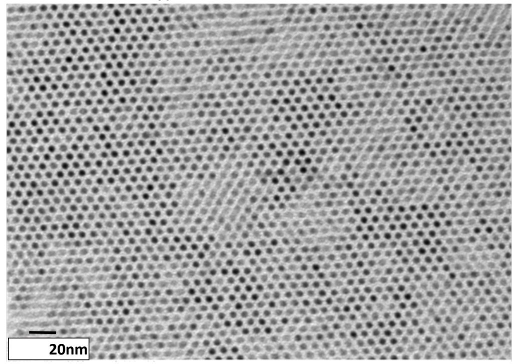
Lab device scale asssembly of nanorod membranes?

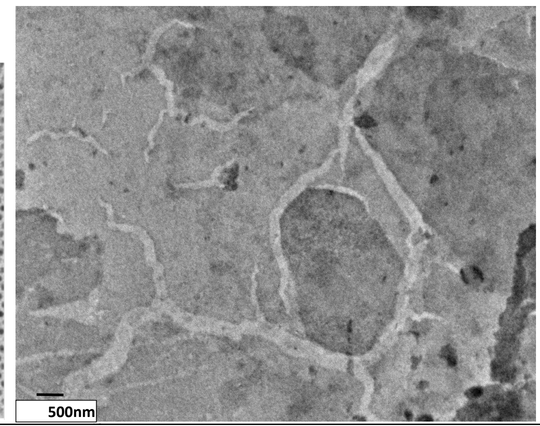




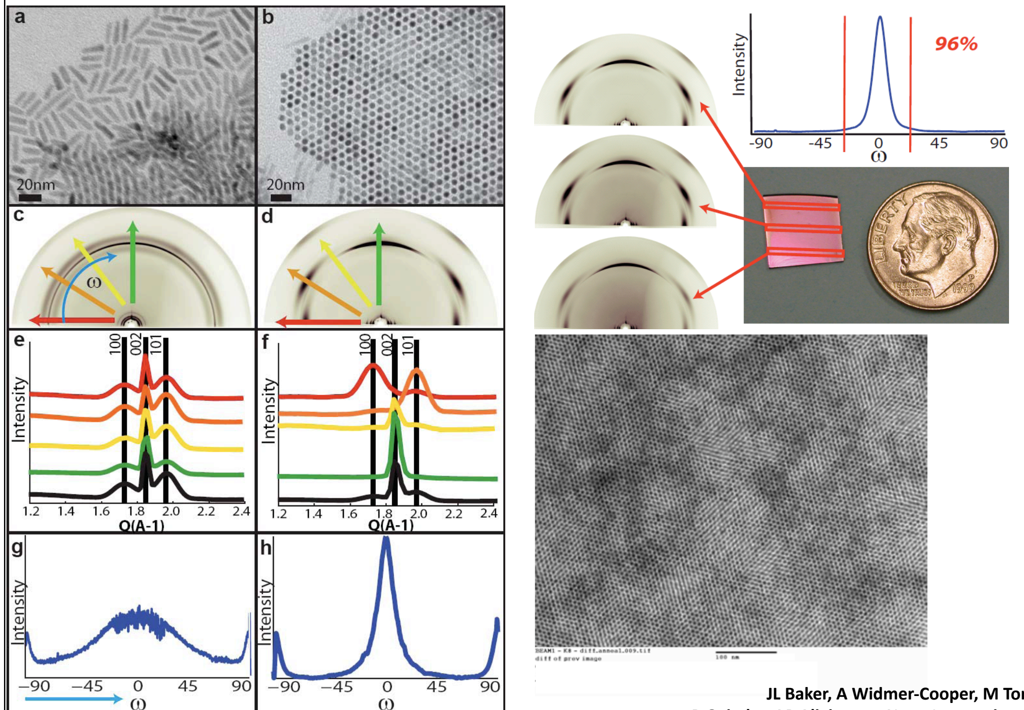
Align Cu_2S/CdS nanorods
with attached metal particles?





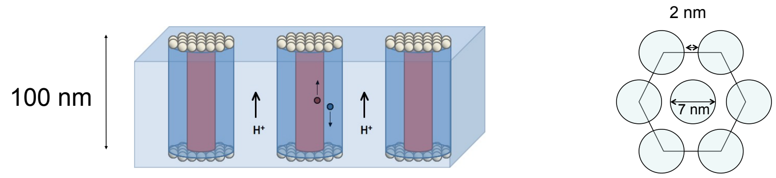


Vertical nanorod alignment on cm scale



JL Baker, A Widmer-Cooper, M Toney,
P Geissler, AP Alivisatos , Nano Letters, in press

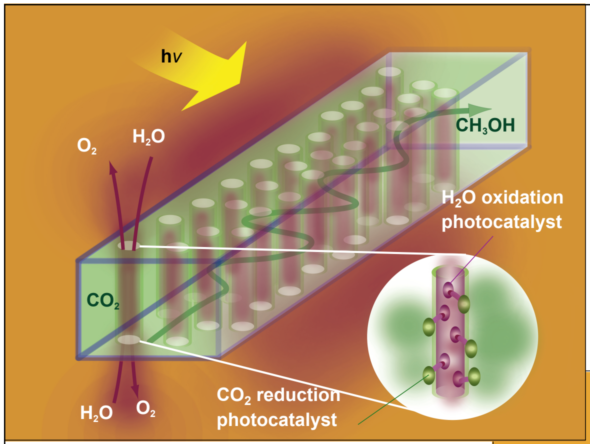
Comparision of rates



Rate Limiting Step	Max H_2 production rate
Solar absorption limiting (1-10% efficiency)	1-10 x 10^{-9} mol H_2 cm^{-2} s^{-1}
Proton diffusion rate (Nafion)	1.1 x 10^{-7} mol H_2 cm^{-2} s^{-1}
Catalyst TOF required to match solar flux	12 s^{-1} nm^{-2}
Worst case Nafion H_2 back diffusion	7.5 x 10^{-11} mol H_2 cm^{-2} s^{-1}

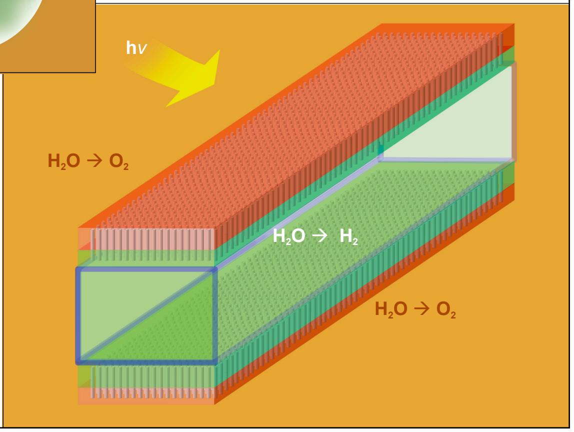
- Solar absorption rate is limiting process, H_2 gas back diffusion substantially lower than H_2 generation rate.

M. Modestino



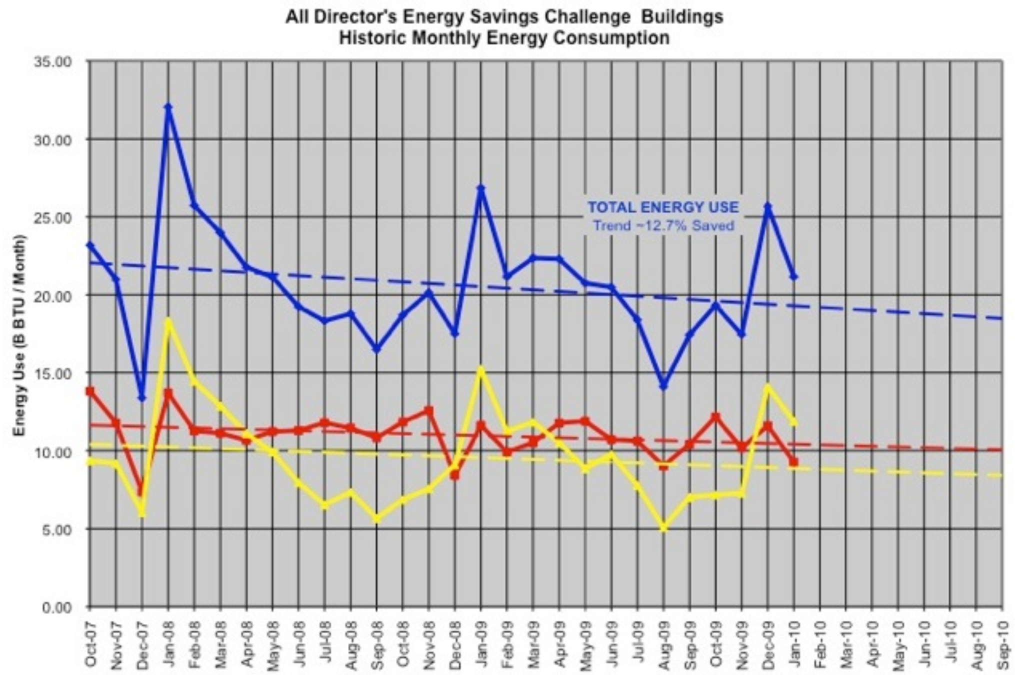
Possible Building Blocks for Scaling up To the Macro Size (30x30 cm)

Subject of a Hub Proposal
Partnering with
Caltech, SLAC, other UC
From LBL: CSD, MSD, PBD Eng



Carbon Cycle 2.0 Initiative

CC2.0 - walk the talk



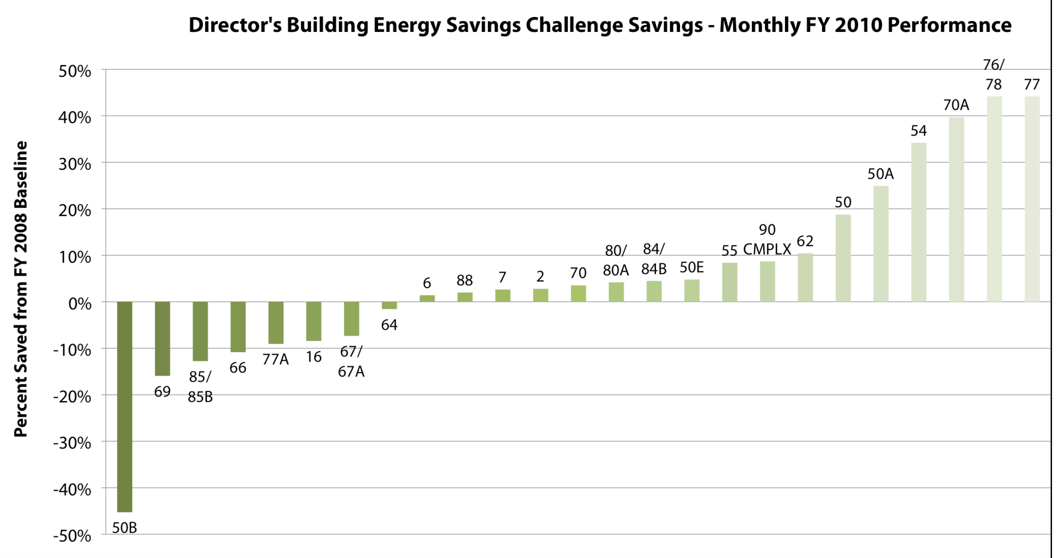
Overall – down in all three cases

Spike in Jan – dates in which we read the meters – longer period representing the jan reading than the nov reading

CC2.0 - walk the talk
Director's Building Energy Savings Challenge

Bldg	Description	Bldg	Description
2	AML	67,67A	Molecular Foundry
6	ALS	69	Ship'g & & Rcvg, Archives, Offices
7	ALS Support	70	Labs, Shops & Offices
16	Labs & Offices	70A	Labs, Shops & Offices
50	Labs, Shops & Offices	76, 78	Facilities Division Offices & Shops
50A	Admin Offices, Labs & Shops	77	EG Shops, Assembly & Labs
50B	Labs, Shops & Offices	77A	Lab & Assembly Facility
50E	Offices	80, 80A	Labs, Shops & Offices
54	Cafeteria	84/84B	Labs & Offices + Utility Building
55	Labs & Research Offices	85, 85B	HWHF
62	Labs, Shops & Offices	88	88 Cyclotron User Facility
64	Labs, Assembly & Offices	90 CMPLX - Offices	
66	Labs & Offices		

Support CC2.0 - Personal Initiative
Director's Building Energy Savings Challenge



Support CC2.0 - Personal Initiative
Director's Building Energy Savings Challenge

- **LBNL Employees challenged to** save energy by changing behavior, to adopt ***personal*** sustainable practices and energy consciousness.
- **The Challenge** – save building energy consumption NOW
  - 25 Onsite buildings and building complexes
  - > 10,000 square feet, with
  - Separately metered energy uses
- **The Rewards** – Saving energy has its own rewards,
  - Monthly Winners: top 3 performing buildings to be announced & highlighted
  - Bi-Annual Winner: building with the most improvement after 6-months: Director will host a BBQ or lunch for **all occupants of the building.**
- **Is it Fair-** No adjustments will be made for renovations: past, in progress, or in the planning stages, nor for accelerating R&D missions

Support CC2.0 - Personal Initiative